THE FORMATION OF NITROGEN

OXIDES IN THE SHOCK WAVE OF A

STRONG EXPLOSION IN AIR

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THE FORMATION OF NITROGEN OXIDES IN THE SHOCK WAVE OF A STRONG EXPLOSION IN AIR

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At high temperatures in the order of several
thousand degrees, an intensive oxygen and nitrogen com-
bination reaction occurs in air, resulting in certain
percentages of the nitrogen being oxidized. The percen-
tage series of nitric oxide which forms is oxidized at
these temperatures to dioxide. The formation of oxides
of nitrogen, especially dioxide which, in contradistinc-
tion to oxygen and nitrogen molecules, strongly absorbs
visible light, is of extremely great significance in
regard to the optical properties of the air in a shock
wave.

It has been found that an entire series of inter-
esting optical phenomena observed during a strong explo-
sion at the stage where the temperature of the wave front
drops from about 7000° to ~1000° owe their origin to the
specific nature of the formation of nitrogen oxides in
the detonation wave and to their optical properties (1).

These phenomena: the incandescence of a shock
wave at the relatively low temperatures of ~7000°-2000°,
the breaking away of the shock wave front from the boun-
dary line of the incandescent body - a fireball at a tem-
perature of the front close to 2000°, the unique effect
of minimum brightness of the fireball at the moment of
breaking away and its further burning are described in
the survey (2).

The starting point for an explanation of these phenomena may be found in an examination of the kinetics of the reactions and the distribution of the concentrations of oxides in the air encompassed by the detonation wave which is the subject of the present work.

Nitric oxide which is formed at high temperatures does not decompose after an explosion when the air cools off, inasmuch as the speed of the reaction drops extremely sharply with a lowering of temperature, the so-called cooling effect takes place. Gradually all of the oxide is oxidized to dioxide. About 100 m of nitrogen oxides in all are formed in an explosion with 10^{21} ergs energy in air. Nitrogen peroxide lends a reddish hue to the cloud rising after the detonation is over, which has been noted in (2). At the stage, of interest to us in this work, where the temperatures are still high, only a small fraction of the oxide is converted to dioxide. This will make it possible to examine the oxide and dioxide formation reactions separately: in the first case disregarding the oxidation of the oxide, and in the second considering the concentration of oxide known.

HYDRODYNAMICS OF AN EXPLOSION AND EQUILIBRIUM CONCENTRATIONS OF NITROGEN OXIDES IN AIR

At the explosion stage which interests us where the temperature of the shock wave front changes from ~7000° to ~1000°, the hydrodynamic process may be describe with good accuracy by the well-known self-modeled solution of the problem of a strong explosion with constant exponent of the adiabatic curve γ, found by L. I. Sedov (3).

According to this solution the distributions of all the hydrodynamic values along the radius depend only on the relation of the radius to the shock wave front radius r/R_ϕ, similarly changing with time. For example, temperature is represented as a function of the coordinate and time in the form:

$$T = T_\phi (t) \cdot \varphi (r/R_\phi) \quad \varphi (1) = 1 \quad (T_\phi \text{ is the}$$

temperature at the front).

The temperature, density and pressure lines for $\gamma = 1.23$ are depicted in Fig. 1.

In actual air the adiabatic exponent at high temperatures depends on temperature and density owing to the excitation of vibrations in the molecules, dissocia-

tion (and ionization when $T > 10000°$). However, as computations of the thermodynamic functions of air with consideration of these processes show, the magnitude of the exponent

$$\gamma = 1 + p/\rho\varepsilon \qquad (1)$$

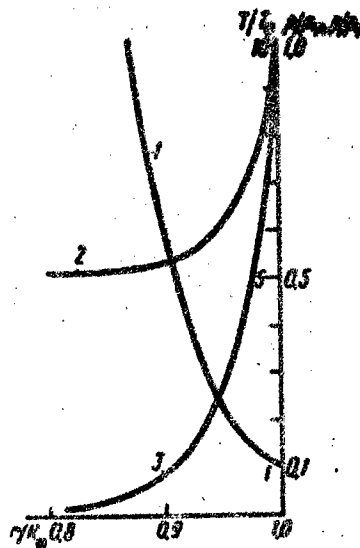varies within rather narrow limits and may be selected in an effective manner.

Fig. 1. Distribution of temperature, pressure and density in a strong detonation wave where $\gamma = 1.23$; 1 – T/T_ϕ; 2 – p/p_ϕ; 3 – ρ/ρ_ϕ

It is precisely the value (1), characterizing the relation of pressure p to the specific internal energy ε (ρ is the density) which determines the hydrodynamic process, and not Poisson's actual adiabatic exponent which in the presence of a variable γ can differ somewhat from value (1) at the very same temperature and density values.

The dissociation of oxygen and nitrogen proceeds very rapidly, so that the concentrations of nitrogen and oxygen atoms and molecules are practically always in equilibrium. As we shall see, this too has bearing on

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the concentration of nitric oxide at temperatures above $\sim 3000°$ (the formation of a small quantity of nitric oxide is barely perceptible in the thermodynamic functions of air), hence the thermodynamic functions can be calculated on the basis of the computation of chemical equilibrium.*.

Table 1 shows ε K Cal/g and exponent γ for certain values of temperature and compression $\eta = \rho/\rho_o$ ($P_o = 1.25 \cdot 10^{-3}$ cm^{-3} is the density of the initial air).

Table 1

ε, K Cal/g $\qquad\qquad\qquad\qquad$ γ

η	ε, ккал/з			$\gamma - 1 + p/\rho\varepsilon$		
	10	1	0,1	10	1	0,1
273°	0,047	0,047	0,047	1,400	1,400	1,400
1000°	0,183	0,183	0,183	1,375	1,375	1,375
2000°	0,412	0,412	0,413	1,335	1,335	1,335
3000°	0,687	0,710	0,771	1,300	1,295	1,295
4000°	1,06	1,22	1,48	1,265	1,240	1,210
6000°	1,99	2,28	2,70	1,235	1,220	1,195
8000°	3,14	4,30	6,52	1,220	1,180	1,145

Generally speaking, to derive the hydrodynamic solution the effective exponent γ should be specifically chosen for each moment of time.

Nevertheless, to shorten numerical computation, it is possible without any particular loss of accuracy to limit the two values $\gamma = 1.23$ with the temperature at the shock front $7000° > T_{\frac{s}{}} > 3000°$ and $\gamma = 1.30$ where $3000° > T_{\frac{s}{}} > 1500°$. The laws of adiabatic cooling and

* In these calculations we have used the energy of
   nitrogen dissociation which is equal to 9.76 electron
volts which, judging by subsequent data (4), is more
probable than the other assumed value of 7.38 e.v.

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the distribution of air particles in the detonation wave computed by the self-modeled solution approximate well the formulas which are convenient for the calculation of the kinetics of the nitrogen oxidation reaction:

$$1/T = 1/T_0 + a/T_0 \ln(t/t_0); \tag{2}$$

$$\eta_i = \eta_{i0}(t_0/t)^{2b}, \tag{3}$$

where T_0 and η_0 - are the temperature and compression at the moment of time t_0 when the shock front crosses the particle, and a and b are the numerical constants which depend solely on the effective exponent γ.

The need to examine the kinetics of the reaction arises only at low shock front temperatures of $3000° > T_{\phi} > 1500°$. At this stage $\gamma = 1.30$ and $a = 0.44$, $b = 0.75$.

Table 2

η	$(c_{NO}) \cdot 10^2$			$(c_{NO_2}) \cdot 10^4$		
	10	5	1	10	5	1
2000°	0,80	0,80	0,80	1,11	0,79	0,35
2600°	2,76	2,75	2,75	2,02	1,42	0,63
3000°	4,66	4,65	4,60	2,24	1,58	0,69
3500°	7,53	7,27	6,96	2,91	1,92	0,79
4000°	9,77	9,51	8,47	2,86	1,90	0,67
5000°	12,21	11,0	7,50	2,11	1,29	0,25

Table 2 lists the values of equilibrium concentrations of NO and NO_2 in air (c_{NO}) and (c_{NO_2}), where the concentration is determined as the relation of the number of molecules of a given sort in a unit mass of air to the number of molecules in a unit mass of cold air. The equilibrium constant of nitrogen peroxide is calculated by the statistical method

$$K_{NO_2} = \frac{p_{NO_2}}{p_{NO}p_{O_2}^{1/2}} = \frac{1,06}{T^{1/4}} \frac{(1 - e^{-2740/T})(1 - e^{-2270/T})^{1/2} e^{8460/T}}{(1 + e^{-174/T})(1 - e^{916/T})(1 - e^{-1060/T})(1 - e^{-2310/T})} \tag{4}$$
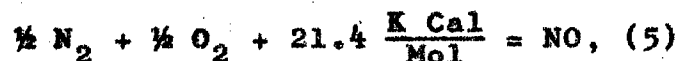
(T in degrees, the partial pressures p_i in atmospheres).

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The heat of reaction and the numerical coefficient were chosen on the basis of a comparison with Bodenstein's experimental data (5) at temperatures from 499 to 825° K, as this had been done by Giauque (6).

The frequency of natural molecular oscillations and the electron energy of the NO molecule were taken from (7).*

THE KINETICS OF NITRIC OXIDE FORMATION IN A DETONATION WAVE

Shock front temperatures of $\sim 7000°$ – $1500°$ are reached at the moment of time $t \sim 10^{-3} - 10^{-1}$ sec for a very wide energy range of the explosion $E \sim 10^{21} - 10^{24}$ erg (3) **. In order to determine how much oxide is formed during this time in the different parts of the air, it is necessary to examine the kinetics of the nitrogen oxidation reaction

$$\tfrac{1}{2} N_2 + \tfrac{1}{2} O_2 + 21.4 \frac{K\ Cal}{Mol} = NO, \quad (5)$$

which is described by the equation

$$\frac{d}{dt} \eta c_{NO} = k \eta^2 \left[(c_{NO})^2 - c^*_{NO}\right], \quad (6)$$

where c_{NO} – is the actual oxide concentration, and (c_{NO}) – is the equilibrium concentration corresponding to the values of nitrogen and oxygen concentrations, to the temperature and the compression at the moment t, which is equal with great accuracy to

$$(c_{NO}) = \frac{8}{\sqrt{3}} \sqrt{c_{N_2} c_{O_2}} e^{-10780/T}. \quad (7)$$

* It should be noted that in the widely distributed handbook (7) the equilibrium constants of K_{NO_2} which were borrowed from the erroneous work of Zeise (8) have been increased by 2.42 times.
**According to the law of analogy the moments corresponding to the given shock wave amplitude $t \sim E^{1/3}$.

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This reaction which proceeds by chain mechanism

$$O + N_2 = NO + O, \quad N + O_2 = NO + O$$

was studied in detail both theoretically and experimentally by Ya. B. Zel'dovich, P. Ya. Sadovnikov and D. A. Frank-Kamenetskiy (9).

The formula which we have derived for the velocity of the reaction, upon being rewritten in our denotations, takes on the form:

$$k = \frac{1.05 \cdot 10^{11}}{\sqrt{\eta c_{O_2}}} e^{-43000/T}. \tag{8}$$

It is evident from formula (6) that the characteristic time for determining the equilibrium concentration of the oxide is *

$$\tau_{NO} = \frac{1}{k(c_{NO})\eta} = \frac{2.06 \cdot 10^{-12}}{\sqrt{\eta c_{N_2}}} e^{53750/T} \quad sec. \tag{9}$$

At temperatures below 5000° the nitrogen barely dissociates and in (9) one can substitute $c_{N_2} = 0.79$.

The values of τ_{NO} for certain temperatures and normal density are presented in Table 3. τ_{NO} increases exceptionally sharply with a reduction in temperature through the great reaction activation energy.

Table 3

$T°, K$	1700	2000	2100	2300	2600	3000	4000
$\tau_{NO}, ce\kappa$	140	1.0	0.27	$3.1 \cdot 10^{-2}$	$2.2 \cdot 10^{-3}$	$1.4 \cdot 10^{-4}$	$1.5 \cdot 10^{-6}$

We will examine the distribution of oxide concenttion behind the wave front at a certain moment of time t Figures 2 and 3 systematically depict the shock

* Actually, under constant outside conditions the solution of equation (6) with the initial condition t = 0, $c_{NO} = 0$ is $c_{NO} = (c_{NO})(e^{2t/\tau_{NO}}-1)/(e^{2t/\tau_{NO}} + 1)$.

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front trajectory and certain air particles and cooling curves of these particles. Allowing that particle A_i was heated by the wave front at moment t_{oi} to temperature $T_{\phi i}$; at moment t it cools adiabatically to temperature T_i. In those particles for which $t - t_{oi} \gg \tau_{NO}(T_i)$ the concentration of oxide is closer, obviously, to equilibrium, since it "follows" from the very beginning behin temperature and density variations which take place slowly in this particle in comparison with the rate of the reaction.

On the contrary, in particles rather close to the front, for which $t - t_{oi} \ll \tau_{NO}(T_{\phi i})$, the oxide does not succeed in forming at the moment t.

It is apparent from a comparison of the characteristic time the particle remains in the heated state $t - t_{oi} \sim t$, which is in the order of $10^{-3} - 10^{-1}$ sec. with the relaxation time τ_{NO} that in the air particles whose temperature is higher than $\sim 3000°$, the concentration of oxide is definitely in equilibrium, while in particles which the front heats to a temperature lower than $\sim 2000°$, the oxide generally never forms. These temperature limits owing to the extremely strong relation $\tau_{NO}(T)$ are very stable and depend merely logarithmically on the force of the explosion.
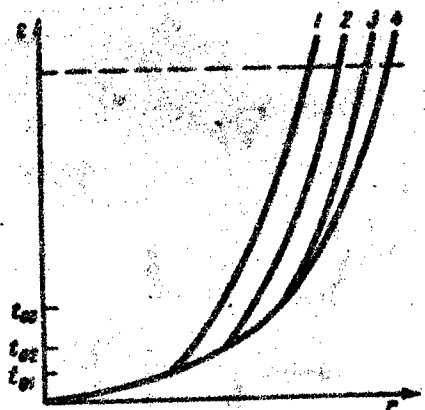

Fig. 2. Schematic illustration of
the trajectories of the shock
front and air particles in a
strong explosion: 1 - A_1; 2 -
A_2; 3 - A_3; 4 - shock front

In the cooling air particles which were heated by the front to a temperature above $\sim 3000°$, the concentration of oxide "follows" the cooling and expansion, remaining near equilibrium only up to a temperature of $\sim 2300°$. Upon reaching a temperature of this order,

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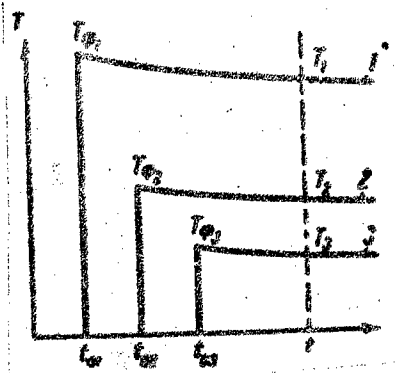Fig. 3. The dependence of
temperature on time
in the air particles
heated by the shock
front of a strong
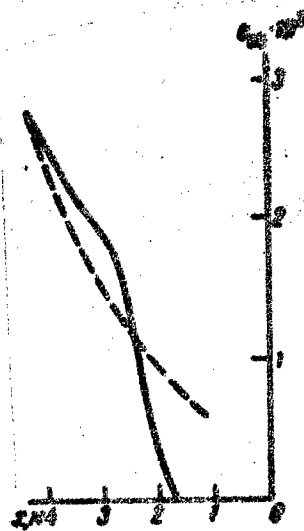explosion: 1 - A_1;
2 - A_2; 3 - A_3

Fig. 4. Distribution of nitric oxide con-
centration behind the shock front at
the moment $t=2.64 \cdot 10^{-2}$ sec, $R_\phi=128$ m;
$T_\phi=1600°$ ($E=10^{21}$ erg). The dotted
line shows the equilibrium concentra-
tion of oxide. Temperatures and pres-
sures are indicated at several points
$x=0$, $T_\phi=1600°$, $\eta_\phi=7.7$; $x=2$m; $T=2010°$,
$\eta=5.8$; $x=4$ m, $T=2550°$, $\eta=4.4$

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further cooling by several hundred degrees practically stops the reaction, and the oxide occurring in the particle at this moment "never" decomposes at this point, despite the fact that according to the law of chemical equilibrium its concentration should be continuously diminishing in proportion to the cooling of the air (the cooling effect).

Inasmuch as at these low temperatures (c_{NO}) is nearly independent of density, the total amount of nitrogen oxidized in the blast is approximately equal to the equilibrium concentration (c_{NO}) at $T \sim 2300°$, multiplied by the quantity of nitrogen in the air encompassed by the detonation wave, where the temperature at the front $T_\phi \sim 2300°$. This value is by dint of similarity proportional to the energy of the explosion and does not depend on air density, i.e. on the height of the explosion (when $E \sim 10^{21}$ erg, as has already been mentioned above, there form ~ 100 m of nitrogen oxides). To compute concentration c_{NO} in the intermediate area for which $t - t_{0i} \sim \tau_{NO} (T_\phi i)$ it is necessary to solve the kinetic equation (6), (7), (8) with the cooling and expansion laws (2), (3). We introduce the new variables

$$x = B\,(t_{0i}/t)^x; \quad y = Bc_{NO}/(c_{NO})_0, \tag{10}$$

where

$$B = [k_0 \eta_0 (c_{NO})_0 t_0 / x]^{1/(5-\delta)}, \quad x = \frac{10750a}{T_0}, \quad \delta = \frac{1+b}{a}.$$

The values with the index zero refer to the initial moment t_0 at which the shock front passed through the particle. The kinetic equation (6) assumes the form

$$\frac{dy}{dx} = x^{3-\delta}(y^2 - x^2), \tag{11}$$

and the initial condition $t = t_0$, $c_{NO} = 0$ is converted to the condition $x = B$, $y = 0$. As may be seen from an estimate, in the interval of change of all the magnitudes of interest to us, it is possible to omit the value δ in the exponent of degree at x in formula (11) without incurring great error.

The Riccati type equation * thus obtained figures in monograph (9) where tables are given which make it possible to plot the integral curve passing through the required point.

Knowing from the hydrodynamic solution the initial conditions t_0, T_0 and η_0 for any particle behind the front, the distribution of c_{NO} behind the front can be computed by the method indicated.

The typical distribution of the oxide behind the shock front at the moment of time the temperature at the front is below 2000° is shown in Fig. 4, in which x is the coordinate read off from the front to the inside of the wave.
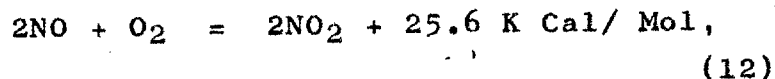
It is evident from the graph that when x < 1.7 m, oxide generally cannot be formed, when x > 4.5 m it is practically in equilibrium. In the layer 4.5 m > x > 1.7 m the concentration of oxide is above equilibrium (cooling effect).

At temperatures of the front above ∼3000° the oxide is at equilibrium throughout, with the exception of the very thin layer immediately behind the front. Thus, for instance, when T_ϕ = 3000° the thickness of the layer around the wave front, within which the oxide has still not yet been able to form, totals 1 cm.

THE KINETICS OF NITROGEN PEROXIDE FORMATION

Differing from the reaction of nitrogen oxidization the nitrogen peroxide formation reaction has been studied experimentally only under comparatively low temperatures.

The well known trimolecular exothermic reaction

$$2NO + O_2 = 2NO_2 + 25.6 \text{ K Cal/ Mol,}$$
(12)

described by the kinetic equation

$$\frac{d}{dt}\eta c_{NO_2} = k'\eta^2 [(c_{NO})^2 - c^2_{NO_2}],$$
(13)

* Resulting in this by means of the corresponding selecttion of variables is the equation of kinetics with the cooling law of the type $1/T=(1/T_0)+(a'/T_0)t$, examined in the book (9). As A.S. Kompaneyets has noted, this equation is integrated in Bessel functions of the order 2/5.

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has a low activation energy and takes place at low temperatures as well.

The rate of reaction of dioxide formation (direct reaction) $(k1')$ cm^6/mol^2 sec. was computed by Glesston by the activated complex method (10). Since the formula for $(k1')$ is derived from very general considerations and is in good accordance with the experimental data of Bodenstein (5) in the temperature range from 353 to 845° K, it can be expected that it will not produce significant errors at the high temperatures which are of interest to us.

The characteristic time of determining equilibrium can be expressed by this rate and the equilibrium constant K_{NO_2}, which is given by formula (4)

$$\tau'_{NO_2} = \frac{1}{k'(c_{NO_2})\eta} = \frac{1,892 \cdot 10^6 T K^2_{NO_2}}{(k_1')\eta(c_{NO_2})} \quad sec. \tag{14}$$
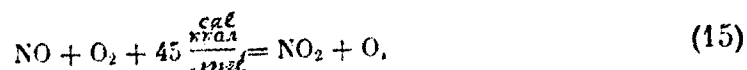
The relaxation times τ_{NO_2} sec. computed according to this formula are presented in Table 4.

Table 4

τ'_{NO_2} a and τ''_{NO_2} b in seconds

η	10		5		1	
τ	τ'_{NO_2}	τ''_{NO_2}	τ'_{NO_2}	τ''_{NO_2}	τ'_{NO_2}	τ''_{NO_2}
1600°			$3,2 \cdot 10^{-2}$	0,35	0,36	0,69
1800°			$1,4 \cdot 10^{-2}$	$3,9 \cdot 10^{-2}$	0,16	$0,9 \cdot 10^{-1}$
2000°	$2,7 \cdot 10^{-3}$	$3,1 \cdot 10^{-3}$	$7,8 \cdot 10^{-3}$	$4,5 \cdot 10^{-3}$	$8,7 \cdot 10^{-2}$	$1,0 \cdot 10^{-2}$
2300°	$5,7 \cdot 10^{-4}$	$2,7 \cdot 10^{-4}$	$1,6 \cdot 10^{-3}$	$4,0 \cdot 10^{-4}$	$1,8 \cdot 10^{-2}$	$0,9 \cdot 10^{-3}$
2600°	$1,9 \cdot 10^{-4}$	$4,4 \cdot 10^{-5}$	$5,4 \cdot 10^{-4}$	$6,3 \cdot 10^{-5}$	$6,1 \cdot 10^{-3}$	$1,4 \cdot 10^{-4}$
3000°	$0,7 \cdot 10^{-4}$	$6,6 \cdot 10^{-6}$	$1,9 \cdot 10^{-4}$	$9,4 \cdot 10^{-6}$	$2,2 \cdot 10^{-3}$	$2,1 \cdot 10^{-5}$
4000°	$1,0 \cdot 10^{-7}$	$2,8 \cdot 10^{-7}$	$3,0 \cdot 10^{-7}$	$4,0 \cdot 10^{-7}$	$4,2 \cdot 10^{-6}$	$1,0 \cdot 10^{-6}$

It is natural to assume that at high temperatures with reaction (12) there will compete, despite its endothermic character, the bimolecular reaction

$$NO + O_2 + 45 \frac{cal}{mol} = NO_2 + O, \tag{15}$$

which is described by the equation

$$\frac{d}{dt}\eta c_{NO_2} = k''\eta^2 c_0 \left[(c_{NO_2}) - c_{NO_2}\right] \tag{16}$$

with the characteristic relaxation time

$$\tau_{NO_2}'' = \frac{1}{k''\eta c_0}. \tag{17}$$

We have not been successful in locating any works in the literature which contain either theoretical or experimental information on the rate of this reaction, hence we will estimate this here by the activated complex method (10). For the sake of convenience we will start out with the reverse reaction of dioxide decomposition, the specific rate of which (k_2'') $cm^3/sec = k''/n_0$ $(N_0 = 2.67 \cdot 10^{19}$ cm^{-3} -- the number of molecules in 1 cm^3 of cold air).

The method yields for the specific rate the general formula

$$(k_2'') = \zeta \frac{Z^*}{Z_{NO_2} Z_0} \cdot \frac{kT}{h}. \tag{18}$$

Here Z_{NO_2}, Z_0, Z^* are the statistical sums of dioxide, oxygen atoms and the NO_3 complex, where the latter includes one variable degree of freedom (this is replaced by the gradual degree of freedom along the reaction path, the statistical sum of which enters as one of the common multiples in the coefficient kT/h); h and k are the Planck and Boltzmann constants; ζ is the transmission coefficient, ordinarily close to unity (we assume $\zeta = 1$).

Coming into the statistical sum of the complex are a series of unknown constants which we single out in the following manner.

The statistical weight of the electron state $g^* \geqslant 2$, since the complex contains one unpaired electron; we will assume $g^* = 2$. The symmetry factor $\sigma^* = 1$, since the complex is asymmetrical. The mass of the complex is 1.39 times larger than the mass of a NO_2 molecule. Assuming that its dimensions surpass to some extent those of NO_2 we will consider that the average moment of inertia of the complex is 1.5 times larger than the mean moment of the NO_2 molecule.

The natural frequencies of the NO_3 molecule, according to which it might have been possible to determine the frequencies of the complex, are not known.

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It can however be assumed that three higher frequencies are less than the frequencies of the NO_2 molecule, which are equal to $h\nu_{NO_2}/k = 960$, 1960 and 2310°, inasmuch as the bond in the complex is weaker. It is easy to prove that the expression for the rate is not very sensitive at the temperatures in which we are interested to the choice of frequencies in the complex. For the calculation we will take the frequencies $h\nu^*/k = 600°$, 800, 900, 1500 and 2000°.

The activation energy of the reverse reaction ϵ is apparently very small, as often occurs when an atom appears through one of the reagents, of a triatomic molecule rather than bivalent.

It may be thought that we have merely lowered the reaction rate, having taken the value $\epsilon = 10$ K Cal/mol.

Substituting these as well as other known constants in formula (18), we obtain

$$(k_2'') = \frac{1.16 \cdot 10^{-12}}{\sqrt{T}} \frac{\prod\limits_{i=1}^{5} f_i^*}{\prod\limits_{i=1}^{3} f_{NO_2 i}} e^{-5030/T}, \tag{19}$$

where $f = (1-e^{-h\nu/kT})^{-1}$ are the multiples in the statistical sums which correspond to normal fluctuations.

The relaxation times τ_{NO_2}'' sec., calculated according to formulas (17), (19) are collected together in Table 4.

It can be seen from Table 4 that at temperatures above 2000° $\tau_{NO_2}' > \tau_{NO_2}''$ the second reaction proceeds more rapidly and is the primary mechanism for the formation of nitrogen peroxide.

By comparing the relaxation times τ'_{NO_2} and τ''_{NO_2} with the characteristic times of the hydrodynamic process at the stage of interest to us $t \sim 10^{-3} - 10^{-1}$ sec., we can draw the following conclusions.

At temperatures above $\sim 2600°$ both reactions occur so rapidly that even when taking the inaccuracy of the estimates into consideration, one can be confident that nitrogen peroxide is in equilibrium with the oxide and oxygen and "follows" changes in their concentrations, temperature and density.

In the temperature range from $\sim 2600°$ to $\sim 2000°$ the reserve is not very large already, however it may be assumed that here too, chiefly as a result of the second reaction, the dioxide enters into equilibrium with the actual (already non-equilibrium!) concentration of oxide rather quickly.

At temperatures of $\sim 2000-1800°$ the relaxation

times are comparable to the times during which a marked change in the state of the air particle takes place, and at still lower temperatures the latter are even surpassed, hence at $T < 2000°$ the dioxide concentration is not in equilibrium.

Fortunately, in the examination of optical effects only temperatures above $\sim 2000°$ are of interest, so that the need of calculating the kinetics of the dioxide, which also cannot be performed reliably, is alleviated.

One should bear in mind while examining low temperatures that in the air particles heated by the shock wave to a temperature lower than 2000°, there are generally no oxides, and consequently, no dioxides.**After this "cooling" nitric oxide slowly oxidizes to dioxide, whereupon as a result of expansion * the rate of this reaction rapidly drops.

The total conversion of nitric oxide to dioxide takes place after the explosion, when the residual heat in the air diffuses as a result of convection; this process lasts a comparatively long while.

I extend my sincere thanks to D.I. Blokhintsev and Ya. B. Zel'dopich for valuable discussions.

CONCLUSIONS

1. The examination of the kinetics of formation reactions of nitrogen oxides and the distribution of their concentrations in the detonation wave are of great value in interpreting the optical phenomena observed during a strong explosion.

2. Equilibrium concentrations of nitric oxide and nitrogen peroxide in air at temperatures of from 2000° to 5000° have been calculated.

3. The kinetics of nitrogen oxidation have been analyzed. A method is given for solving the kinetic equation in adiabatically cooling air particles in the detonation wave. It was shown that at temperatures above 3000° the concentration of oxide is in equilibrium, at temperatures below 2300° the cooling effect takes place. In air layers encompassed by the shock front with a

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* The adiabatic cooling of air is small; for instance, a particle with the temperature of 2000° and pressure of 50 atm. with the pressure dropping to that of the atmosphere, i.e. upon reconversion to the normal state, cools off totally to 750° ($T \sim p^{(\gamma-1)/\gamma}$, $\gamma \approx 1.35$) expansion is very great ($\rho \sim p^{1/\gamma}$); the particle expands ~ 20 times.

** See next page for insert

In particles which were first heated to higher temperatures and adiabatically cooled and expanded, the dioxide "following" the oxide decomposes up to temperatures of $\sim 2000°$.

temperature below $\sim 2000°$, generally oxide is not formed. The total quantity of nitrogen oxidized in the explosion was estimated.

   4. The kinetics of dioxide formation are examined. It was shown that at temperatures above $\sim 2000°$ a basic role is assumed, not by the ordinary trimolecular reaction, but by the reaction $NO + O_2 = NO_2 + O$. The rate of the reaction was computed by the activated complex method. It was demonstrated that at temperatures above $\sim 2000°$ the dioxide is in equilibrium with the oxide.

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THE FORMATION OF NITROGEN OXIDES IN THE SHOCK WAVE OF A STRONG EXPLOSION IN AIR

Yu. P. Raizer (Moscow)

Summary

In the report the kinetics are examined of the formation of the nitrogen oxides NO and NO_2 and their distribution is calculated in air caught in a strong shock wave. An estimation is made of the total nitrogen oxidized during the strong explosion.

It has been shown that the nitrogen oxide does not form in fronts with temperatures below 2000°.

The basic mechanism in the formation of the dioxide at temperatures above 2000° has been shown to be the process $NO + O_2 = NO_2 + O$ and the rate of this reaction has been calculated with the aid of the activated complex method.

The investigation was necessary to explain a number of optical phenomena observed in a strong explosion: glow of the shock wave at temperatures 7000—2000, the breaking away of the wave front from the ball of fire and the characteristic intensity minimum of the latter. An interpretation of these effects has been given by the author in another report [1].

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